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In re Application of:

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Application No. 09/636,246

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For: POLISHING SYSTEM WITH STOPPING COMPOUND AND METHOD OF ITS USE

Group Art Unit: unassigned

Examiner: unassigned

PRELIMINARY AMENDMENTS TO SPECIFICATION AND CLAIMS

(deletions indicated by crossed-out text; additions indicated by underlined text)

Amendments to the paragraph beginning at page 1, line 14:

Integrated circuits are made up of millions of active devices formed in or on a substrate, such as a silicon wafer. The active devices are chemically and physically connected into a substrate and are interconnected through the use of multilevel interconnects to form functional circuits. Typical multilevel interconnects comprise a first metal layer, an interlevel dielectric layer, and sometimes a third and subsequent metal layer. Interlevel dielectrics, such as doped and undoped silicon dioxide (SiO_2) and/or low-κ ~~dielectrics are~~ dielectrics, are used to electrically isolate the different metal layers.

Amendments to the paragraph beginning at page 5, line 19:

The polishing additive can be any suitable phosphorous-containing compound. Suitable phosphorous-containing compounds include, for example, phosphates (e.g., pyrophosphates, tri-phosphates, condensed phosphates), phosphonic acids (e.g., mono-phosphonic acids, di-phosphonic acids, tri-phosphonic acids, poly-phosphonic acids), and salts of phosphonic acids. Preferred phosphorous-containing compounds include, for example, pyrophosphates, phosphonoacetic acid, ~~ethylene di-phosphonic~~ ethylenediphosphonic acid, 1-hydroxyethylidene-1,1-~~di-phosphonic~~ diphosphonic acid, and mixtures thereof. Preferred phosphorous-containing compounds also include, for example, $M_n^{+1}H_{3-n}PO_4$ and $M_m^{+1}H_{4-m}P_2O_7$, wherein M^{+1} is a cationic species (e.g., Na, K, Cs, Rb, NH_4^+), ~~n= 0-3~~ n = 0-3, and m = 0-4. Moreover, a preferred phosphorous-containing compound is R-O-PO_3, wherein R is an organic moiety selected from the group consisting of alkyl, aryl, cyclic, and aromatic groups having from 1-18 carbon atoms.

Amendments to the paragraph beginning at page 6, line 1:

Preferably, at least one polishing additive comprises the structure ~~XY-NCR^{1}R^{2}CR^{3}R^{4}N-X'Y'~~ XY-NCR^{1}R^{2}CR^{3}R^{4}N-X'Y', wherein X, Y, X', Y', R^1, R^2, R^3, and R^4 are ~~selected from~~ selected from the group consisting of hydrogen (H) atoms, heteroatom-containing functional groups, alkyl groups, heteroatom-containing alkyl groups, cyclic groups, heteroatom-containing cyclic groups, aromatic groups, heteroatom-containing aromatic groups, and combinations thereof. More preferably, at least one polishing additive comprises the structure ~~XY-NCR^{1}R^{2}CR^{3}R^{4}N-X'Y'~~ XY-NCR^{1}R^{2}CR^{3}R^{4}N-X'Y', wherein X and X' are H atoms, and wherein Y, Y', R^1, R^2, R^3, and R^4 are selected from the group consisting of hydrogen (H) atoms, heteroatom-containing functional groups, alkyl groups, heteroatom-containing alkyl groups, cyclic groups, heteroatom-containing cyclic ~~groups, aromatic~~ groups, aromatic groups, heteroatom-containing aromatic groups, and combinations thereof. Even more preferably, at least one polishing additive comprises the structure ~~XY-NCR^{1}R^{2}CR^{3}R^{4}N-X'Y'~~ XY-NCR^{1}R^{2}CR^{3}R^{4}N-X'Y', wherein X, Y, X', and Y' are H atoms, and wherein R^1, R^2, R^3, and R^4 are selected from the group consisting of hydrogen (H) atoms, heteroatom-containing functional groups, alkyl groups, heteroatom-containing alkyl groups, cyclic groups, heteroatom-containing cyclic groups, aromatic groups, heteroatom-containing aromatic groups, and combinations thereof. In this regard, nitrogen-containing compounds that consist of primary amine groups are preferred over nitrogen-containing compounds that comprise secondary amine groups and/or tertiary amine groups, alone or in combination with primary amine groups. Moreover, it is suitable for at least one polishing additive to comprise the structure as described above, wherein the structure is in the form of a polymer comprising about four or more (e.g., about 10 or more, about 15 or more, about 20 or more, about 30 or more, about 40 or more, or even about 50 or more) dissimilar, similar, or even identical adjoined structures. Most preferably, the nitrogen-containing compound is selected from the group consisting of polyethylenimine, 1,3-diamino-2-propanol, ~~imino-di-acetic acid~~ imino-diacetic acid, 2-amino-1-butanol, ethylenediamine, aminoethylethanolamine, ~~2,2'-aminoethoxy-ethanol~~ 2,2'-aminoethoxyethanol, and mixtures thereof.

Amendments to the paragraph beginning at page 7, line 18:

Suitable polishing additives also include one or more compounds selected from the group consisting of (i) compounds that are both phosphorous-containing compounds and nitrogen-containing compounds, (ii) compounds that are both phosphorous-containing compounds and sulfur-containing compounds, (iii) compounds that are both nitrogen-containing compounds and sulfur-containing compounds, and (iv) compounds that are phosphorous-containing compounds, nitrogen containing compounds, and

sulfur-containing compounds. Preferred polishing additives include, for example, compounds selected from the group consisting of ~~2-aminoethyl phosphonic~~ 2-aminoethylphosphonic acid, amino(trimethylenephosphonic acid), ~~diethylenetriaminepenta(methylene phosphonic acid)~~ diethylenetriaminepenta(methylenephosphonic acid), ~~hexamethylenediamine tetra(methylene phosphonic acid)~~ hexamethylenediaminetetra(methylenephosphonic acid), and mixtures thereof. Moreover, preferred polishing additives include, for example, phosphonic compounds containing primary, secondary and/or tertiary amines, such as, for example, ~~N-(phosphonomethyl) iminodiacetic acid~~ N-(phosphonomethyl)iminodiacetic acid, 2-aminoethyl dihydrogen phosphate, ~~2-aminoethyl phosphonic acid~~ 2-aminoethylphosphonic acid, ~~2-aminoethyl phosphonic acid~~ 2-aminoethylphosphonic acid, aminotri(methylenephosphonic acid) (i.e., Dequest® 2000 product), ~~1-hydroxyethylidene-1, 1-di-phosphonic acid~~ 1-hydroxyethylidene-1,1-diphosphonic acid (i.e., Dequest® 2010 product), and ~~diethylenetri-aminepenta(methylenephosphonic acid)~~ diethylenetriaminepenta(methylenephosphonic acid) (i.e., Dequest® 2060 product).

Amendments to the paragraph beginning at page 8, line 16:

The stopping compound can be any suitable cationically charged nitrogen-containing compound selected from the group of compounds comprising amines, imines, amides, imides, polymers thereof, and mixtures thereof. The term "cationically charged" as used herein means that a portion (e.g., about 5% or more, about 10% or more, about 15% or more, or about 20% or more) of the stopping compound in the liquid portion of the system is in cationic form at the operating pH of the system of the present invention. Preferably, the stopping compound has a pKa value that is 1 or more units greater than the operating pH of the liquid portion of the system. For example, in a system with a pH of 6.5, preferred stopping compounds would have a pKa value of about 7.5 or more. Preferred stopping compounds also are oppositely charged from the surface charge of the second layer of the substrate layer. Suitable stopping compounds include, for example, compounds comprising primary amines, secondary amines, tertiary amines, quaternary amines (i.e., quaternary ammonium salts), etheramines, oligomeric amines, oligomeric imines, oligomeric amides, oligomeric imides, polymeric amines, polymeric imines, polymeric amides, polymeric imides, or mixtures thereof. Moreover, suitable stopping compounds include, for example, amino acids, amino alcohols, amino ether alcohols, or mixtures thereof. Preferred stopping compounds also include, for example, polyetheramines, polyethylenimines, ~~N_4-amino (N,N'-bis-[3-aminopropyl]ethylene diamine)~~ N_4-amino(N,N'-bis-[3-aminopropyl]ethylenediamine), 4,7,10-trioxatridecane-1,13-diamine, ~~3,3-dimethyl-4,4-diaminodicyclo-hexylmethane~~

3,3-dimethyl-4,4-diaminodicyclohexylmethane, 2-phenylethylamine, ~~N,N-dimethyldi propylenetriamine~~ N,N-dimethyldipropylenetriamine, 3-[2-methoxyethoxy]propylamine, dimethylaminopropylamine, ~~1,4-bis(3-aminopropyl) piperazine~~ 1,4-bis(3-aminopropyl)piperazine, and mixtures thereof. In addition, preferred stopping compounds include, for example, isophorone diamine, hexamethylenediamine, ~~cyclohexyl-1,3-propane diamine~~ cyclohexyl-1,3-propanediamine, thiomicamine, ~~(aminopropyl)-1,3-propane diamine~~ (aminopropyl)-1,3-propanediamine, ~~tetraethylene pentamine~~ tetraethylenepentamine, tetramethylbutanediamine, propylamine, diaminopropanol, aminobutanol, (2-aminoethoxy)ethanol, or mixtures thereof.

Amendments to the paragraph beginning at page 9, line 10:

The system of the present invention can comprise any suitable combination of at least one polishing additive and at least one stopping compound. For example, the system can comprise polyethylenimine and at least one polishing additive selected from the group consisting of a carboxylic acid (preferably, a di-, tri-, or poly-carboxylic acid), a phosphate (preferably, a pyrophosphate, a tri-phosphate, or a condensed phosphate), an acid thereof, and a phosphonic acid (preferably, a di-, tri-, or poly-phosphonic acid). The system also can comprise at least one polishing additive selected from the group consisting of a carboxylic acid (preferably, a di-, tri-, or poly-carboxylic acid), a phosphate (preferably, a pyrophosphate, a tri-phosphate, or a condensed phosphate), an acid thereof, and a phosphonic acid (preferably, a di-, tri-, or poly-phosphonic acid) and at least one stopping compound comprising two or more, three or more, four or more, five or more, or even six or more nitrogen atoms (e.g., at least one stopping compound comprising two or more amine groups, at least one stopping compound comprising two or more primary amine groups, at least one stopping compound comprising two or more amino groups and 4 or more carbon atoms, or at least one stopping compound comprising two or more primary amine groups containing 3 or more carbon atoms). Moreover, the system can comprise at least one polishing additive selected from the group consisting of a carboxylic acid (preferably, a di-, tri-, or poly-carboxylic acid), a phosphate (preferably, a pyrophosphate, a tri-phosphate, or a condensed phosphate), an acid thereof, and a phosphonic acid (preferably, a di-, tri-, or poly-phosphonic acid) and a quaternary ammonium salt comprising the structure $NR^1R^2R^3R^4$, wherein R^1, and R^2 are methyl groups and R^3 and R^4 are selected from the group consisting ~~of of hydrogen~~ of hydrogen (H) atoms, heteroatom-containing functional groups, alkyl groups, heteroatom-containing alkyl groups, cyclic groups, heteroatom-containing cyclic groups, aromatic groups, heteroatom-containing aromatic groups, and combinations thereof. In addition, the system can comprise at least one polishing additive selected from the group

consisting of a carboxylic acid (preferably, a di-, tri-, or poly-carboxylic acid), a phosphate ~~acid~~ (preferably, a pyrophosphate, a tri-phosphate, or a condensed phosphate), an acid thereof, and a phosphonic acid (preferably, a di-, tri-, or poly-phosphonic acid) and at least one stopping compound comprising an aminopropyl group and/or at least one stopping compound having a molecular weight (MW) of about 80 or more (e.g., a MW of about 100 or more, a MW of about 250 or more). Furthermore, the system can comprise a peroxide, aminotri(methylenephosphonic acid), and ~~1, 4-bis(3-amino propyl) piperazine~~ 1,4-bis(3-aminopropyl)piperazine, and optionally, at least one passivation film forming agent comprising one or more 5-6 member heterocyclic nitrogen-containing rings. The system also can comprise a peroxide, tartaric acid, and a polyethylenimine, and, optionally, at least one passivation film forming agent comprising one or more 5-6 member heterocyclic nitrogen-containing rings.

Amendments to the paragraph beginning at page 11, line 34:

The system of the present invention further can comprise a source of ammonia (e.g., ammonia or an ammonium salt). Ammonia and/or ammonium salts enhance the removal rate and/or removal selectivity (e.g., Cu:Ta removal selectivity) of the system, by interacting with one or more components of the system (e.g., the polishing additive). Preferably, the system of the present invention comprises ammonia and/or ammonium salts and one or more polishing additives. Preferably, the system comprises a source of ammonia and at least one polishing additive selected from the group consisting of a carboxylic acid (preferably, a di-, tri-, or poly-carboxylic acid), a phosphate (preferably, a pyrophosphate, a tri-phosphate, or a condensed phosphate), an acid thereof, and a phosphonic acid (preferably, a di-, tri-, or poly-phosphonic acid). For example, the system can comprise ~~aminotri(methylene-phosphonic acid)~~ aminotri(methylenephosphonic acid) and a source of ammonia (e.g., ammonia and/or an ammonium salt).

Amendments to the paragraph beginning at page 12, line 9:

Suitable polymeric compounds include, for example, any suitable polymeric compound that reduces the polishing rate of at least one layer associated with the substrate. Preferably, the system comprises at least one polymeric compound comprising a polyvinylalcohol, a polyethylene oxide, a polypropylene oxide, a sulfonic acid polymer, a sulfonate polymer, or a mixture thereof.

Amendments to the paragraph beginning at page 18, line 5:

Copper wafers, tantalum wafers, and silicon dioxide (SiO_2) wafers were polished separately with fourteen different polishing compositions with 3 wt.% alumina (specifically, Cabot's Semi-Sperse® W-A355 product), 2.5 wt.% oxidizing agent (specifically, H_2O_2), 1 wt.% polishing additive (specifically, ammonium oxalate ($(NH_4)_2C_2O_4$)), and varying concentrations of a stopping compound (specifically, 0.2 wt.% ~~isophorone diamine~~ isophoronediamine, 0.2 wt.% ~~hexamethylene diamine~~ hexamethylenediamine, 0.2 wt.% N-cyclohexyl-1,3-~~propane diamine~~ propanediamine, 0.2 wt.% N-(3-aminopropyl)-1,3- ~~propane diamine~~ propanediamine, 0.2 wt.% tetraethylenepentamine, 0.2 wt.% N,N,N',N'-tetramethyl-1,4-butanediamine, 0.5 wt.% propylamine, 0.2 wt.% 2-(2-aminoethoxy)ethanol, 2.0 wt.% 1,3-diamino-2-propanol, 1.0 wt.% thiomicamine, 3.0 wt.% 2-amino-1-butanol, 0.2 wt.% 4,7,10-trioxa-1,13-tridecanediamine, 0.2 wt.% lysine, 0.2 wt.% ~~poly[bis(2-chloroether)-alt-1,3-bis(3-dimethylamino)propyl]~~) poly[bis(2-chloroether)-*alt*-1,3-bis(3-dimethylamino)propyl], wherein each of the systems had a pH of 7.6. For comparison purposes, the test wafers also were polished with a control system ("control") with 3 wt.% alumina (specifically, Cabot's Semi-Sperse® W-A355 product), 2.5 wt.% oxidizing agent (specifically, H_2O_2), and 1 wt.% polishing additive (specifically, ammonium oxalate $(NH_4)_2C_2O_4$), wherein the control system had a pH of 7.6. Following use of the polishing compositions, the relative tantalum (Ta) removal rate and the relative silicon dioxide (SiO_2) removal rate of each system were determined in comparison with the removal rates of the control system, with the resulting data set forth in Table 3.

Table 3:

System	Stopping Compound	Relative Removal Rate Ta	Relative Removal Rate SiO_2
Control	none	1	1
3A	0.2 wt.% ~~isophorone diamine~~ isophoronediamine	0.17	-
3B	0.2 wt.% hexamethylenediamine	0.24	0.27
3C	0.2 wt.% ~~N-cyclohexyl-1,3-propane diamine)~~ N-cyclohexyl-1,3-propanediamine	0.12	0.11
3D	0.2 wt.% N-(3-aminopropyl)-1,3-propanediamine	0.17	0.03